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FULL LENGTH ARTICLE

Mercury and tin contents in water and sediments along the Mediterranean shoreline of Egypt

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Abstract Surface seawater and surficial sediment samples were collected from the Egyptian Mediterranean beach during May 2010 to study the impact of land-based activity on the distribution of mercury and tin. Hg and Sn were analyzed by using Hydride system MH10 coupled with atomic absorption spectrophotometer. The obtained data indicated that Nile Delta, Port Said and Alexandria beaches, which are the most industrialized areas in the Egyptian Mediterranean Sea, showed high levels of mercury in water compared to other studied sites. These areas receive huge amounts of wastes from many sources. Sinai side and north coast beaches could be used as reference sites, as they are almost uncontaminated without harmful outfalls. In the same context, Alexandria beach showed the absolute high level of tin in water (1.225 μg/l), while the minimum level was recorded at Port Said area (0.226 μg/l). On the other hand, the highest mean value of Hg in sediments (14.938 ng/g) was found in Sinai Beach and Sn (1.414 μg/g) was at Alexandria beach. ANOVA analysis was used to show the difference in the concentration of Hg and Sn in water and sediments throughout the different studied Parts. Also correlation coefficient was calculated to show the relationship between Hg and Sn in water and sediments of the investigated area.

Introduction

Pollution is the most serious of all-environmental problems and posses a major threat to the health and well-being of millions of people and global ecosystems. In recent years, pollution becomes a paramount problem with increasing the human activities. Heavy metals considered to be one of the most common and effective pollutants for the marine life which have severe environmental impact on all organisms.

Mercury is one of the most harmful pollutants in the marine environment (Araujo et al., 1996). Its concentration in the

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global environment is significantly increasing and reaching levels of potential (lethal and sub lethal) toxicity for many living organisms (Wagemann et al., 2000). It is included in the list of high priority environmental contaminants within the Convention for the Protection of the Marine Environment of the North East Atlantic (OSPAR Convention), the International European Union Water Framework Directive (EUWFD) and the United States Environmental Protection Agency (USEPA) (Palma et al., 2009). Concentrations of mercury in most marine waters fall within the range of 0.05–0.19 μg/l (Robertson, 1972). Accordingly, Mediterranean Sea was considered to be relatively higher in Hg concentration than the Pacific Ocean (Cossa et al., 2004; Horvat et al., 2003; Kotnik et al., 2007; Sunderland and Mason, 2007).

Tin occurs naturally in the earth's crust with a concentration of approximately 2–3 ppm (Budavari, 2001). Tin compounds are found in various environmental media in both inorganic and organic forms. It may be released to the environment from natural and anthropogenic sources, and is a component of many soils and inorganic tin compounds may be released in dusts from wind storms, roads, and agricultural activities (WHO, 1990; Senesi et al., 1999). Unlike the organotin, the inorganic tin did not receive adequate study in the Mediterranean area. Yemeniciğlu et al. (1987), Aksu et al. (1997) and Arambarri et al. (2003) had been investigated the inorganic tin in sediments at different sites in the Mediterranean Sea.

Mediterranean Sea is a semi-closed basin connected to the world oceans through the narrow and shallow Strait of Gibraltar (Shobier et al., 2011). Some of the Egyptian coastal areas of the Mediterranean Sea (especially in front of the large cities) receive different types of pollution sources. Therefore, the present work is carried out to assess the direct impact of land based activities on the occurrence of Hg and Sn in water and sediments along the Egyptian Mediterranean shoreline.

Materials and methods

Study area

Egyptian Beaches of the Mediterranean Sea was divided into five parts, which selected to cover all the area under investigation (Fig. 1).

Part I (Sinai beach): includes five locations called (M1) 5 km east of El-Arish, (M2) infront of El-Arish, (M3) 10 km west of El-Arish, (M4) south of Lake Bardawil, and (M5) Mediterranean coast-west of Lake Bardawil.

Part II (Port Said beach): includes five locations called (M6) east of Suez Canal, (M7) west of Suez Canal, (M8) west of Port Said, (M9) eastern connection of Lake Manzala–Mediterranean, and (M10) western connection of Lake Manzala–Mediterranean.

Part III (Nile Delta beach): includes nine locations called (M11) infront of Damietta branch, (M12) 0.5 km west of Damietta branch, (M13) Ras El-Bar beach, (M14) Damietta harbour, (M15) Gamasa beach, (M16) east of Lake Burullus, (M17) Baltim beach, (M18) infront of Rashid beach, and (M19) infront of Edku beach.

Part IV (Alexandria beach): includes eleven locations called (M20) Abu Qir Bay, (M21) El-Maamora beach, (M22) infront of Sheraton El-Montazah, (M23) infront of Sedi Beshr, (M24) infront of Keliobatra beach, (M25) east of eastern harbour, (M26) west of eastern harbour, (M27) western harbour, (M28) El-Mex Bay, (M29) El-Dekhaila harbour, and (M30) El-Agamy beach.

Part V (North beach): includes eight locations called (M31) Maraqia beach (50 km west of Alexandria), (M32) El-Hamam, (M33) El-Alamien, (M34) El-Dabaa, (M35) Alam El-Rom (15 km east of Mersa Matruh), (M36) infront of Mersa Matruh, (M37) Keliobatra beach (open sea), and (M38) Keliobatra lagoon.

Seawater analysis

Surface seawater samples were collected by using water sampler during May 2010 at 38 sites along the Egyptian Mediterranean beaches (Fig. 1). Concentrations of mercury and tin were determined according to standard methods (APHA, 1989). Hg and Sn were detected by flameless and flame atomic absorption spectrophotometer (AAS) using cold vapor technique stripping by an argon flow, the metallic Hg and Sn were reduced by sodium borohydride. The determination was performed using Perkin Elmer Aanalyst 100 atomic absorption spectrophotometer equipped with MHS-10 mercury/hydride system. Chemicals used for the standard solutions and reagents were of the highest purity. Deionized bidistilled water was used throughout the work.

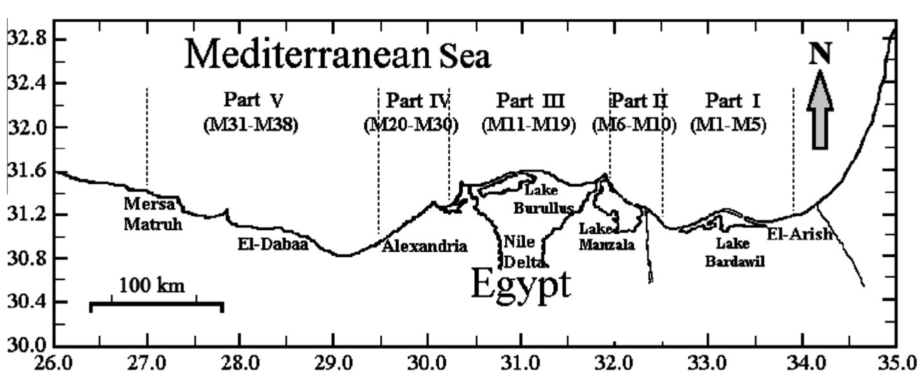

Figure 1 Map of the Egyptian Mediterranean shoreline showing the selected parts and locations. (Part I: Sinai beach, Part II: Port Said beach, Part III: Nile Delta beach, Part IV: Alexandria beach, and Part V: North coast beach.)

Sediments analysis

Thirty-seven surficial sediment samples were collected by using a grab sampler at the same sites and time of seawater samples. For Hg determination, 0.5 g of the dried sample was heated in a water bath at 95 °C with aqua-regia and further addition of 5% solution of $KMnO_4$, $K_2S_2O_8$ and NaCl–$(NH_4{\cdot}OH)_2H_2SO_4$ consequently (EPA, 1983). Then, Hg concentration was determined by flameless AAS using the cold vapor technique. For tin determination, digestion of dried sample was determined by adding a mixture of nitric and perchloric acids (3:1) in a Teflon crucible (EPA, 1983). Sn concentration was determined by flame AAS. Blanks were provided through all determinations. The precision and accuracy for the method of metals determination in seawater and sediments were checked by replicate measurements of the Hg and Sn in the same sample. Precision was found satisfactory which was in the range of 9.4–21.0% for the two metals.

The statistical analyses of the present data were conducted using computer program: STATISTICA for windows (Release 4.5, Copyright© StatSoft, Inc. 1993).

Results and discussion

Seawater

It is cited from the literature that the main anthropogenic sources of Hg and Sn for marine environment are: (a) river run-off carrying wastes discharged into the river system, (b) wastes discharged directly into the marine environment, either as discharges as liquid effluents or through dumping (e.g. solid wastes, sewage sludge) and (c) atmospheric inputs specially of Hg (GESAMP, 1985). Marine water have been shown to contain concentrations of Hg from less than 0.03 up to of 0.20 μg/l, but most marine waters fall within the range of 0.05 to 0.19 μg Hg/l (Robertson, 1972). Smith and Burton (1972) reported an average concentration of Sn in surface water of eastern Atlantic Ocean of 0.01 μg/l.

Table 1 shows the distribution of Hg and Sn in the shoreline seawater of the Egyptian Mediterranean Sea. The absolute maximum of surface Hg concentration was 2.877 μg/l recorded at location M17 (Nile Delta beach). Such concentration is an indicator of high land activities. While, the absolute minimum value is 0.600 μg/l which was found at location M36 (North Coast beach) as expected to be virtually unpolluted. On the other hand, the absolute maximum concentration of Sn in surface seawater was 1.225 μg/l recorded at location M24 (Alexandria beach). While, the minimum value was 0.226 μg/l recorded at location M8 (Port Said beach).

Data of Hg and Sn concentrations in seawater were statistically estimated to find the correlation coefficient between these two metals. The results of the relationship showed that there is insignificant correlation between Hg and Sn ($r = 0.154$, at $p < 0.05$).

Fig. 2 shows the variations of Hg and Sn in seawater throughout the different parts of the Egyptian Mediterranean beaches. It is evidenced that the mean concentrations of Hg were somewhat high at Nile Delta beach (Part III), followed by Port Said beach (Part II) and Alexandria beach (Part IV), then Part (V) of the North Coast beach and Part (I) of Sinai beach. However, these variations exhibited insignificant differences at confidence limit 95% when processed using ANOVA analysis. Nile Delta, Port Said and Alexandria beaches are the most industrialized areas in the Mediterranean (Egypt) and received huge amounts of wastes from different sources, therefore they showed high levels of Hg comparing to the others area (North Coast and Sinai beaches) which are relatively far away from the pollution sources. In the same context, Alexandria beach showed the higher level of Sn through all the investigated area. For Sn, ANOVA analysis showed significant difference ($p < 0.05$) between Parts I: IV and V, and between Parts II: IV.

Referring to the situation of the sampling sites, the high levels of Hg and Sn were found in sites suffering from different pollution sources, such as industrial effluents, sewage drains, tourist activities, harbors, ship waiting areas and high populations areas. Muller et al. (1989) stated that the areas around marinas had high levels of Sn, where antifouling paints is used. WHO (1980), UNEP (1985) and FAO (1992) reported that the main sources of Hg and Sn in the marine environment were industrial effluents as pigments and paints, catalysts, dental and cosmetics, glass, batteries and other electricals, alloys and solders, fertilizers, plastics and fuel factories, agricultural effluents having biocides and fertilizers, domestic effluents and mining effluents. Some of these sources already exist in the present study area, particularly at the locations M17, M16, M24 and M12, which had higher concentrations of Hg and Sn than other locations.

By comparing the concentration of Hg and Sn in seawater of the present study and those recorded in other areas which have the same environmental conditions (Forstner and Wittmann, 1979; Aboul-Dahab, 1985; Hamed, 1996; El-Moselhy et al., 1998; El-Moselhy and Hamed, 2000; Abd El-Azim, 2002). It can be noticed that the present concentrations were higher than those found in other regions. As well as, Hg and Sn in seawater of the present study were higher than the background concentration, which were <10–30 ng Hg/l (Moore, 1991) and 0.01 μg Sn/l (Forstner and Wittmann, 1979). This result indicated that the present investigated area is suffered from pollution by Hg and Sn.

Sediments

Table 1 shows the distribution of Hg and Sn in the beach sediments of the Mediterranean Sea, Egypt. The absolute maximum concentration of Hg in sediment samples was 22.521 ng/g which recorded at location M29 (Alexandria beach), such concentration is an indicator of high land activities. While, the minimum value (8.879 ng/g) was found at location M28. On the other hand, the highest concentration of Sn was recorded at location M26 – Alexandria beach (3.790 μg/g), and the lowest one (0.419 μg/g) was detected at location M19 (Nile Delta beach). According to the mean values of the two studied metals through the different Parts (Fig. 3), it can reported that the highest mean value of Hg (14.938 ng/g) was found in Sinai beach while Sn (1.414 μg/g) was in the Alexandria beach. The variations in the concentration of Hg and Sn between the studied parts showed insignificant difference (using ANOVA analysis) at confidence limit 95%. Data of Hg and Sn in sediments throughout the investigated area were statistically tested to obtain the correlation coefficient, which showed insignificant relationship ($r = -0.016$, at $p < 0.5$).

Table 1 Levels of Hg and Sn in coastal seawater and sediments collected from different locations along the Mediterranean shoreline, Egypt.

Part	Location	Hg		Sn	
		Water (μg/l)	Sediments (ng/g)	Water (μg/l)	Sediments (ng/g)
I	M1	0.735	14.153	0.474	1.461
	M2	1.157	13.636	0.332	1.273
	M3	0.961	21.488	0.360	1.661
	M4	0.765	13.740	0.587	0.889
	M5	0.706	11.674	0.488	0.454
	Mean	**0.865**	**14.938**	**0.448**	**1.148**
	±S.D.	**0.194**	**3.785**	**0.103**	**0.481**
II	M6	0.882	11.880	0.326	2.897
	M7	0.902	11.157	0.432	0.725
	M8	0.912	12.397	0.226	0.736
	M9	1.140	13.223	0.554	0.525
	M10	1.105	11.054	0.637	–
	Mean	**0.988**	**11.942**	**0.435**	**1.221**
	±S.D.	**0.124**	**0.902**	**0.166**	**1.122**
III	M11	0.982	–	0.238	–
	M12	0.842	11.880	0.456	–
	M13	0.947	14.050	0.438	0.989
	M14	1.018	13.223	0.431	1.119
	M15	0.877	12.087	0.500	2.673
	M16	1.211	20.021	0.628	–
	M17	2.877	17.810	0.791	1.296
	M18	0.784	12.603	0.786	0.560
	M19	0.882	12.913	0.372	0.419
	Mean	**1.158**	**14.323**	**0.516**	**1.176**
	±S.D.	**0.656**	**2.972**	**0.186**	**0.806**
IV	M20	0.800	10.320	0.631	1.301
	M21	0.950	13.636	1.006	1.626
	M22	0.800	13.120	0.455	0.736
	M23	0.850	11.880	0.700	0.831
	M24	0.925	10.950	1.225	0.942
	M25	1.150	9.886	0.698	1.978
	M26	0.975	12.293	0.645	3.790
	M27	0.975	9.783	0.382	1.419
	M28	0.925	8.879	0.656	1.273
	M29	1.025	22.521	0.651	0.807
	M30	0.650	9.928	0.794	0.854
	Mean	**0.911**	**12.109**	**0.713**	**1.414**
	±S.D.	**0.133**	**3.767**	**0.234**	**0.880**
V	M31	0.825	15.919	0.465	1.437
	M32	0.925	10.955	0.413	0.625
	M33	0.775	12.397	0.626	–
	M34	1.600	12.293	0.665	–
	M35	0.800	12.913	0.681	1.413
	M36	0.600	14.566	0.545	0.495
	M37	0.800	12.190	0.725	0.460
	M38	0.775	11.260	0.607	0.501
	Mean	**0.888**	**12.812**	**0.591**	**0.822**
	±S.D.	**0.301**	**1.666**	**0.109**	**0.471**

Although, levels of Hg and Sn in the sediments are influenced by the human activities, however, three major problems exist in the interpretation of the data concerning the concentrations of trace metals in sediments: (1) The concentration of a metal in sediments is not only a function of the quantity of the metal deposited, but also a function of the rate of metal deposition over a given period of time, (2) The concentration of metal found in sediments depends on the organic content of the sediments, in general, metal increase approximately linearly with increase in the organic content (Halcrow et al., 1973; Hamed and El-Moselhy, 1999), and (3) Other variables such as particles nature, form and size may also affect the concentrations of metal in sediments. In addition, differences in mobilization rates (biological and physical) may lead to erroneous conclusions concerning the rate of metal input. These problems may explain why Hg and Sn were elevated at location

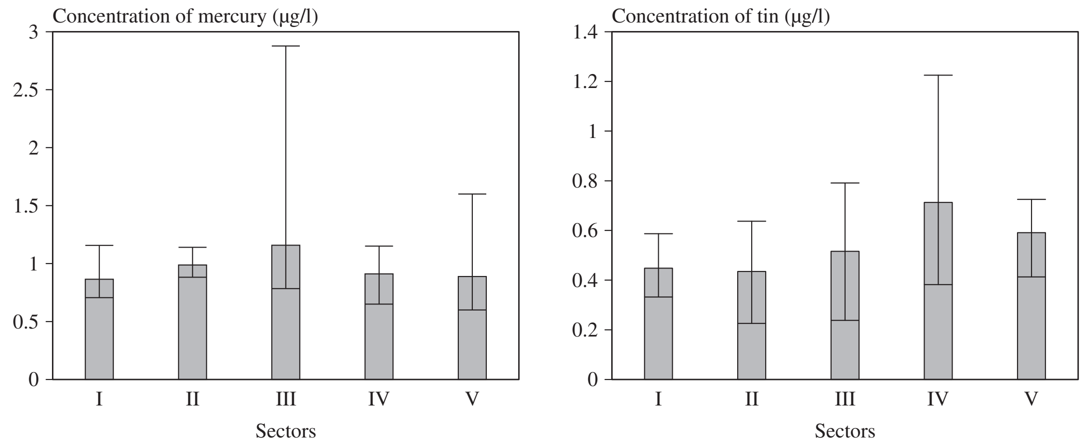

Figure 2 Variations of Hg and Sn in seawater at different Parts of the Egyptian Mediterranean shoreline. (Error bar represents the lowest and highest value for each Part.)

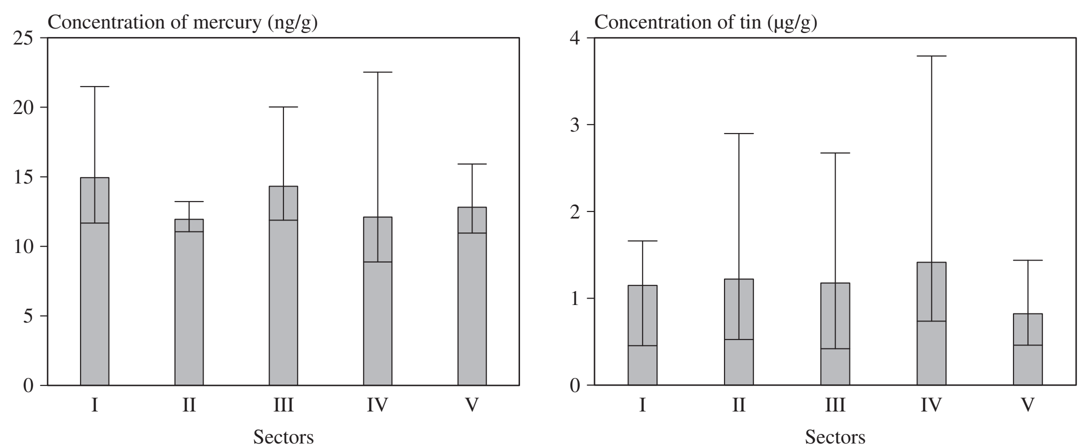

Figure 3 Variations of Hg and Sn in sediments at different parts of the Egyptian Mediterranean shoreline. (Error bar represents the lowest and highest value for each Part.)

Table 2 Concentrations of Hg in sediments of the present investigated area comparing to other studies.

Region	Hg_t conc. (µg/g)	References
Mediterranean, Egypt	0.009–0.023	Present study
Alexandria coast	0.8	El-Sokkary (1978)
Mex Bay	0.01–8.90	Aboul-Dahab (1985)
Arabian Gulf	0.02–0.12	Samhan et al. (1987)
Bay of Bengal	0.75–55.2	Sasamal et al. (1987)
Bombay Island	0.17–7.00	Mahajan and Srinivasan (1988)
Suez Canal	0.063–0.264	Hamed (1996)
Gulf of Suez	0.012–0.150	Hamed (1996)
Aqaba Gulf	0.016–0.047	El-Moselhy and Hamed (2000)
Gulf of Suez	0.012–0.419	El-Moselhy and Hamed (2000)
Red Sea proper	0.018–0.215	El-Moselhy and Hamed (2000)
Suez Canal (Port Said coast)	0.05–0.12	Abd El-Azim (2002)
Alexandria coast	0.03–17.82	Shobier et al. (2011)
Typical concentration	0.1–0.5	Moore (1991)

M1, M3 and M31 which are relatively far away from any human activities or other land sources.

Table 2 shows the concentration of Hg in sediments of the present investigated area comparing to that of other studies (Hamed, 1996, Abd El-Azim, 2002 and Shobier et al., 2011). It is obviously that the present concentration is lower than other levels of Hg as well as the typical concentration which ranged between 0.1 and 0.5 µg/g (Moore, 1991). Limited data

Table 3 Concentrations of Sn in sediments of the present investigated area comparing to other studies.

Region	Snt conc. (μg/g)	References
Mediterranean, Egypt	0.419–3.790	Present study
Turkey Coast	0.17–2.30	Yemeniciğlu et al. (1987)
Lake Mariute	1.875–8.19	Aboul-Dahab et al. (1990)
Izmir Bay, Turkey	>4	Aksu et al. (1997)
Red Sea proper	0.045–0.904	El-Moselhy and Hamed (2000)
Gulf of Suez	0.021–1.183	El-Moselhy and Hamed (2000)
Aqaba Gulf	0.024–0.890	El-Moselhy and Hamed (2000)
Gipuzkoa, Spain	11–113	Arambarri et al. (2003)

were available about levels of total Sn in sediments because most of the studies deal with organotin. Table 3 shows comparison between Sn concentration in sediment in this study and other studies in different areas.

The present data clarifies that the land-based activities are the main pollution problem in the Egyptian shoreline of Mediterranean Sea. It is evidence that the area of investigation can be divided into five parts concerning the concentration of Hg; the mean concentrations of Hg were somewhat high at Nile Delta Bseach, followed by Port Said beach and Alexandria beach, then north coast and Sinai beaches. The concentrations of Hg and Sn in seawater were higher than those found in other areas which have the same environmental conditions as well as the background concentrations. This result showed that the present investigated area is suffered from pollution by Hg and Sn. Therefore, Sinai and North coast beaches of the Egyptian Mediterranean Sea should be developed as the natural recreation areas being far from the industrial development. Furthermore, any industry that cannot recirculate its wastes for the beneficial use of the environment and economy should not be allowed to be established on the Sinai and North coast beaches. However, if beaches on the Mediterranean shoreline are to be saved, strict legislation should be issued for treating wastes before disposal.

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